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Inorganica Chimica Acta

Contents

Articles

Annamaria Camus, Nazario Marsich, Anna Maria Manotti Lanfredi, Franco Ugozzoli, Chiara Massera

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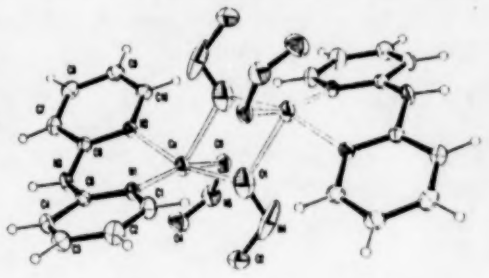
Copper(II)nitrito complexes with 2,2′-dipyridylamine. Crystal structures of the [(acetato)(2,2′-dipyridylamine)(nitrito-*O*,*O*′)copper(II)] and [(2,2′-dipyridylamine) (nitrito-*O*,*O*′)(μ-nitrito-*O*)copper(II)]$_2$·2(acetonitrile)

Some copper(II)nitrito complexes with 2,2′-dipyridylamine (dipyam) were synthesized and the two complexes [Cu(CH_3COO)-(dipyam)(ONO-*O*,*O*′)] (**I**) and [Cu(dipyam)(ONO - *O*,*O*′)(μ - ONO - *O*)]$_2$·2CH_3CN (**II**) were characterized by X-ray diffraction. **I** consists of two crystallographically independent [Cu(acetato)(dipyam)(ONO)] complexes self-assembled by cooperative N–H···O and C–H···O intermolecular interactions in supramolecular tetrameric units. **II** is a rare example of a dimeric nitrito copper(II) derivative containing both *cis*-monodentate and *O*-bridging nitrito ligands.



II

R.W. Eveland, D.F. Shriver

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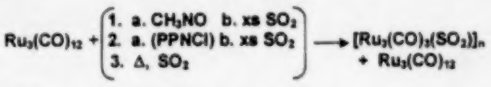
The reaction of tri-ruthenium clusters with sulfur dioxide

The metal carbonyl cluster $Ru_3(CO)_{12}$ was activated for substitution by several different methods. Addition of sulfur dioxide to these activated products yielded two polymeric compounds which have the general formula $[Ru_3(CO)_3(SO)_2]_n$.



Paula M. Secondo, John M. Land, Russell G. Baughman, Harvest L. Collier

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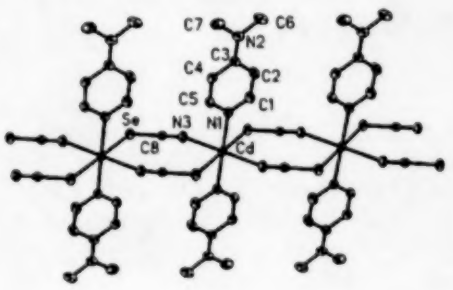
Polymeric octahedral and monomeric tetrahedral Group 12 pseudohalogeno (NCX^-: X = O, S, Se) complexes of 4-(*N*,*N*-dimethylamino)pyridine

A series of Group 12 pseudohalides (OCN^-, SCN^-, $SeCN^-$) containing 4-(*N*,*N*-dimethylamino)pyridine (4-dmap) has been prepared. X-ray diffraction, NMR and IR spectroscopy are utilized to elucidate the nature of pseudohalide coordination. A rare crystallographic example of the polymeric double bridging capability of the selenocynate ion is illustrated by [Cd(SeCN)$_2$(4-dmap)$_2$]$_n$.



Jinfeng Ni, Qingxian Zhou, Diana K. Canseco, Tammy R. Calhoun, Annette R. Graham, Kara L. Carreras, Carolyn N. Schultz

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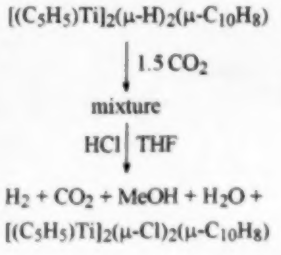
Transformation of carbon dioxide to methoxide by the complex [(C_5H_5)Ti]$_2$(μ-H)$_2$(μ-$C_{10}H_8$)

Hydrogenation of carbon dioxide by the complex (CpTi)$_2$(μ-H)$_2$(μ-$C_{10}H_8$) (**1**) affords a mixture. The protonation of the product mixture reveals that one of the two bridging hydrides in **1** is involved in the hydrogenation of CO_2. The labeling study with DCl in D_2O indicates that the complex **1** transforms CO_2 to methoxide.



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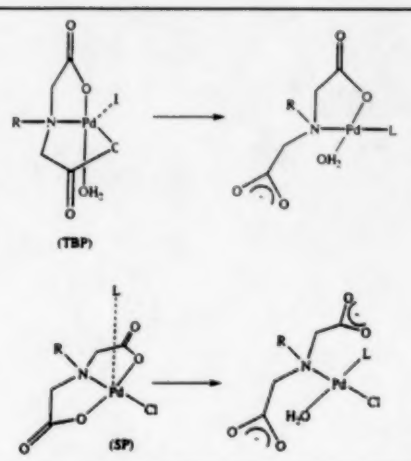
Thomas W. Stringfield, Rex E. Shepherd

Inorg. Chim. Acta 309 (2000) 28

Substitution of inosine and guanosine-5′-monophosphate for chloride, and water on Pd^{II}(polyaminopolycarboxylate) complexes: mechanistic controls in forming Pd^{II}(pac)L or Pd^{II}(pac)L_2 products

The substitution reactions of inosine (Ino) and guanosine 5′-monophosphate (5′-GMP) proceeds at Pd^{II} iminodiacetate-derived complexes, [Pd^{II}(pac)X], by associative interchange intermediates (I_a) that are more trigonal-bipyramidal for $X = H_2O$ and more square-pyramidal for $X = Cl^-$. The more stable products are N-7 coordinated. Presence of one anionic donor, either Cl^- or 5′-GMP causes addition to stop at the first step, forming (Pd^{II}(pac)L] complexes, whereas the species for $X = H_2O$ and neutral Ino substitutions proceed to bis [Pd^{II}(pac)L_2] with identifiable *cis* and *trans* isomers.



Benjamin P. Warner, Joseph A. D'Alessio, Arthur N. Morgan III, Carol J. Burns, Ann R. Schake, John G. Watkin

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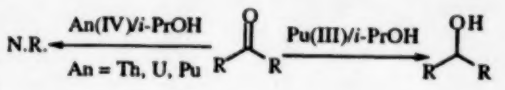
Plutonium(III) - catalyzed Meerwein–Ponndorf–Verley reactions

The reactivity of Th(IV), U(III), U(IV), Pu(III) and Pu(IV) *iso*-propoxide in the Meerwein–Ponndorf–Verley reduction of ketones by *iso*-propanol have been examined and compared with the reactivity of analogous lanthanide and transition metal systems.



Seog Woo Rhee, Yong Hwan Na, Youngkyu Do, Jinkwon Kim

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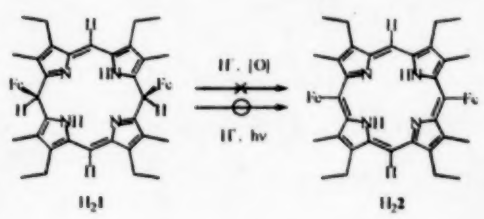
Synthesis, structures and electrochemical characterization of ferrocene-substituted porphyrin and porphodimethene

Large steric bulkiness of ferrocenyl group makes it possible to isolate air-stable porphodimethene H_2**1**. Compound H_2**1** was proved to be an intermediate species of porphyrin H_2**2** in only photooxidation pathway. Two ferrocene subunits of H_2**2** communicate with each other through an extended conjugated π-system, while those of H_2**1** are electrochemically separated.



Evgenia Spodine, Yanko Moreno, María Teresa Garland, Octavio Pena, Ricardo Baggio

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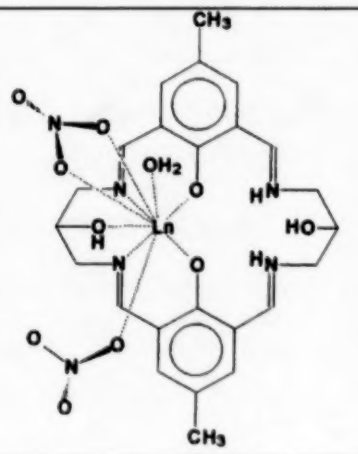
Molecular structure and magnetic properties of $[Gd(LH_4)(NO_3)_2(H_2O)]NO_3(H_2O)_2$, $[Sm(LH_4)(NO_3)_2(H_2O)]NO_3(H_2O)_{1.5}(CH_3OH)_{0.5}$ and $[Cu_2(LH_2)(H_2O)_2](NO_3)_2$ complexes (LH_4: Schiff base ligand derived from 4-methyl-2,6-diformylphenol and 1,3-diaminopropanol)

Mononuclear lanthanide(III) complexes (Ln = Gd (**1**), Sm (**2**), La (**3**)) and the dinuclear copper(II) complex (**4**) of the macrocyclic ligand LH_4 have been prepared. Single crystal X-ray diffraction studies were carried out on **1**, **2** and **4**. ^1H and ^{13}C NMR spectra show the same structure for the La(III) complex **3** as the one determined for **1** and **2**. Magnetic susceptibility data are given for these complexes.



Z.N. Chen, R. Appelt, H. Vahrenkamp

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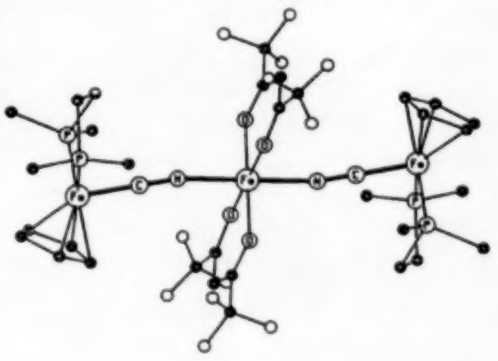
Cyanide-bridged trinuclear complexes based on central bis(hexafluoroacetylacetonate)metal units

The metal hexafluoroacetylacetonates $M(hfa)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd) were combined with metallocyanides L_nM'–CN (M′ = Fe, Ru) to form trinuclear complexes with M′–CN–M–NC–M′ backbones. Their electronic nature was probed by structure determinations and cyclic voltammetry.



Delanie Lamprecht, Gert J. Lamprecht

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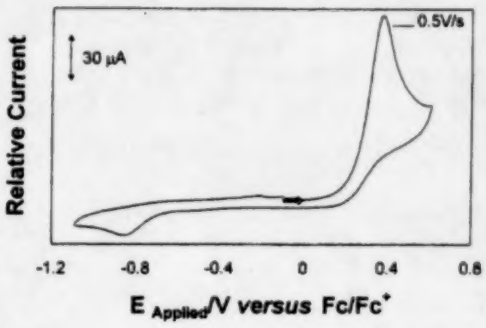
Electrochemical oxidation of Rh(I) to Rh(III) in rhodium(I) β-diketonato carbonyl phosphine complexes

Cyclic voltammetric studies revealed a direct relationship between the irreversible oxidation potentials of Rh(I) to Rh(III) in complexes of the type [Rh(I)(β-diketonato)(CO)(PPh_3)] and the pK_a-values of the free β-diketones dibenzoylmethane, benzoylacetone, benzoyltrifluoroacetone and trifluoroacetone. The effect of different solvents on the reduction potential of these complexes proved solvent co-ordination. An ECE, EC and EE electrochemical mechanism is predicted.



[Rh(dbm)(CO)(PPh_3)]

Marina Cindrić, Neven Strukan, Višnja Vrdoljak, Tihana Fuss, Gerald Giester, Boris Kamenar

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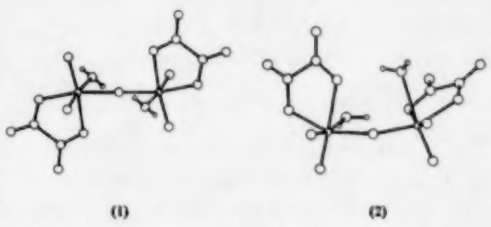
Synthesis and structures of ammonium and tetraphenylphosphonium salts of (μ-oxo-diaquadioxalatotetraoxodimolybdenum(VI). An interesting example of intramolecular hydrogen bonds within the dimeric anion

The reaction of molybdenum(VI) oxide with oxalic acid and RCl where R = NH_4 (**1**) and $(C_6H_5)_4P$ (**2**), results in the formation of molybdenum(VI) oxalate complexes of the general formula $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$. Whereas in the ammonium salt the Mo–O–Mo bridge is linear, that one in the corresponding tetraphenylphosphonium salt is angular with an angle of 162.42(15)° at the oxygen atom, stabilized by intramolecular hydrogen bonds between coordinated water molecules and oxalato-oxygens.



Q. Lu, Alok Singh, Jeffrey R. Deschamps, E.L. Chang

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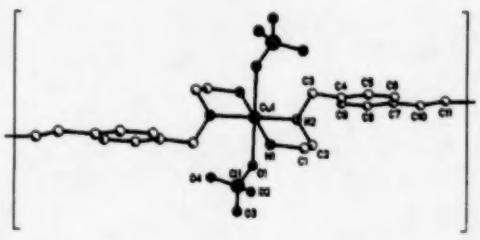
Cu(II)-containing cross-linked polymers for the hydrolysis of 4-nitrophenyl phosphate

Active polymeric catalysts were made from non-reactive monomeric complexes. The Cu(II)-containing cross-linked polymers made by incorporating $[Cu(L1)_2]X_2$ (*N*-(4-vinyl)benzyl ethylenediamine (**L1**)) and $[Cu(L3)_2]X_2$ (4-(4-vinyl)benzyl diethylenetriamine (**L3**)) catalyze the hydrolysis of 4-nitrophenyl phosphate with first-order rate constants of 1.33×10^{-5} and 1.04×10^{-6} s^{-1}, respectively, at 55°C and pH 8.5. The crystal structures of two of the metal centers are also reported.

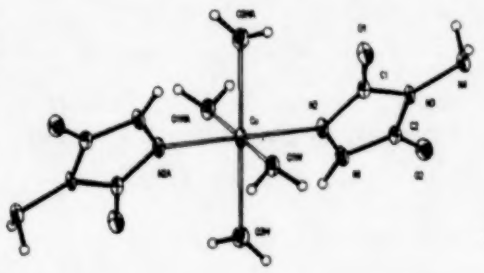


Diego Alberto Gianolio, Maurizio Lanfranchi, Francesco Lusardi, Luciano Marchiò, Maria Angela Pellinghelli

Inorg. Chim. Acta 309 (2000) 91

Synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 4-amino-1,2,4-triazolidine-3,5-dione (urazine)

The complexing capability of urazine, 4-amino-1,2,4-triazolidine-3,5-dione as neutral (Hur) or monoanionic (ur) ligand was investigated towards divalent cations (Co, Ni, Cu, Zn). Several compounds were synthesized and the crystal structures of $CoCl_2(Hur)_2 \cdot 4H_2O$ (**1**), $Zn(SO_4)(Hur) \cdot 2H_2O$ (**3**), $Cu_3(NO_3)_2(ur)_4 \cdot 6H_2O$ (**8**), $Cu(ur)_2 \cdot 4H_2O$ (**9**), $Cu_2(SO_4)(ur)_2 \cdot 2H_2O$ (**10**) were determined by X-ray diffraction methods. Hur acts only as *N,O* chelating agent in **1** and **3**, whereas ur acts as monodentate through the deprotonated triazolidine nitrogen atom in **9** or as tridentate in **8** or tetradentate in **8** and **10**.



Gregg J. Lumetta, Bruce K. McNamara, Brian M. Rapko, Richard L. Sell, Robin D. Rogers, Grant Broker, James E. Hutchison

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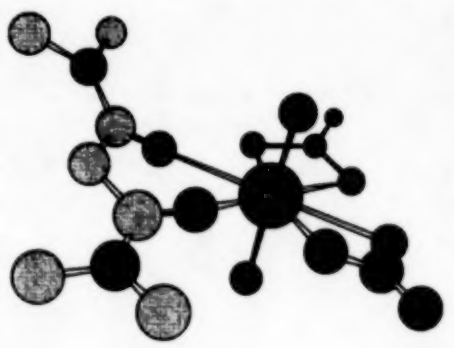
Synthesis and characterization of mono- and bis-(tetraalkylmalonamide)uranium(VI) complexes

The complex $[UO_2(NO_3)_2(TMMA)]$ (TMMA = *N,N,N′,N′*-tetramethylmalonamide) was structurally characterized by single-crystal X-ray diffraction. The complexes $[UO_2(THMA)_2](BF_4)_2$(THMA = *N,N,N′,N′*-tetrahexylmalonamide) and $[UO_2(TMMA)_2](OTf)_2$ (OTf = triflate) were also prepared. Comparison of the FTIR spectra of these complexes to the spectra of complexes formed in liquid–liquid extraction systems supports the hypothesis that complexes of the type $[UO_2(NO_3)_2L]$ and $[UO_2L_2](NO_3)_2$ form in the extraction systems.

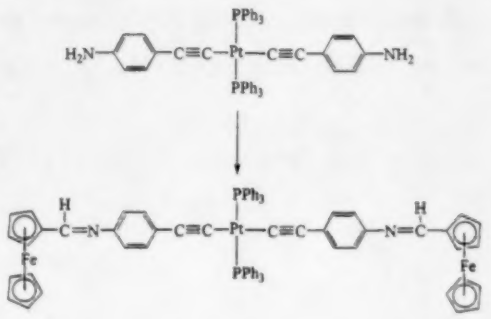


Antony J. Deeming, Graeme Hogarth, Mo-yin (Venus) Lee, Malini Saha, Simon P. Redmond, Hirihattaya (Taya) Phetmung, A. Guy Orpen

Inorg. Chim. Acta 309 (2000) 109

para-Ethynyl aniline as a building block for fully π-conjugated ligands and acetylide complexes: crystal structures of *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4NH_2)_2]$ and $[(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}C{\equiv}CC_6H_4NH_2)]$

para-Ethynyl aniline has been used to prepare new π-conjugated ligands and acetylide complexes such as *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4NH_2)_2]$, which in turn has been used to synthesise extended chain complexes with amide, imine, imino-phosphorane and ferrocenyl imine units.



John W. Babich, Wendy Graham Coco, Sandra Barrow, Alan J. Fischman, Frank J. Femia, Jon Zubieta

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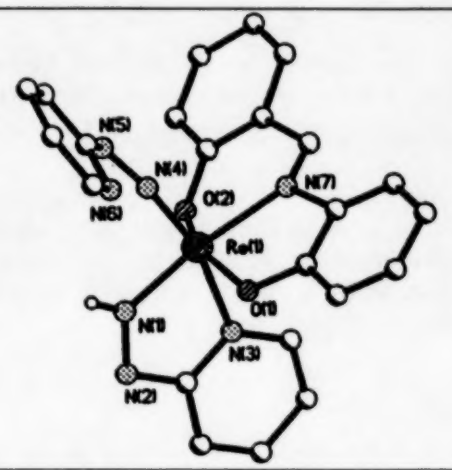
^{99m}Tc-labeled chemotactic peptides: influence of coligand on distribution of molecular species and infection imaging properties. Synthesis and structural characterization of model complexes with the $\{Re(\eta^2\text{-}HNNC_5H_4N)(\eta^1\text{-}NNC_5H_4N)\}$ core

The identity of the coligand can have a profound influence on the biodistribution of ^{99m}Tc-HYNIC-conjugated peptides. For the coligand set, mannitol, glucamine, glucarate, tricine and glucoheptonate, ^{99m}Tc-mannitol-HYNIC peptide has the most favorable combination of concentration in infected tissue, T/B ratio and biodistribution in uninfected tissues. However, the complex structural chemistry of the Tc-hydrazino-coligand complex results in product mixtures, an observation confirmed by model studies, which also suggest that more rigid ONO donor sets are more appropriate. The model complex $[Re(OC_6H_4C(H){=}NC_6H_4O)(NNC_5H_4N)(HNNC_5H_4N)]$ illustrates this point.



Beom-Sang Yoo, Nam-Sun Choi, Chang Yong Shim, Yongkeun Son, Soon W. Lee

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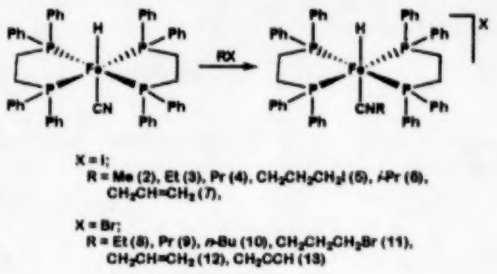
Electrophilic attack of alkyl halide at the cyanide nitrogen in *trans*-$[Fe(H)(CN)(dppe)_2]$: preparation, structure, and properties of *trans*-$[Fe(H)(CNR)(dppe)_2]X$ ($dppe = Ph_2PCH_2CH_2PPh_2$; R = Me, Et, Pr, *i*-Pr, *n*-Bu, CH_2CH_2Br, $CH_2CH_2CH_2I$, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$; X = Br, I)

Dissolution of *trans*-$[FeH(CN)(dppe)_2]$ in various alkyl halides (RX: X = Br or I) under argon led to the formation of complexes of the type *trans*-$[FeH(CNR)(dppe)_2]X$. In these reactions, alkyl halides behave both as reagents (electrophiles) and solvents. Molecular structure of compounds **5** and **13** show that the M–H hydrogen (or halide) in both compound appears to be dihydrogen-bonded simultaneously to the two C–H bonds.



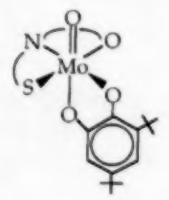
Notes

Jalal U. Mondal, Jesus G. Zamora, Merritt D. Kinon, Franklin A. Schultz

Inorg. Chim. Acta 309 (2000) 147

Six-coordinate monooxo molybdenum(VI) complexes with catecholate and salicylaldehyde thiosemicarbazone ligands

Six-coordinate MoO(Mecat)(PhTSCsal) and MoO(DTBcat)(PhTSCsal) are formed by coordination of tridentate $PhTSCsal^{2-}$ and bidentate catecholate to MoO^{4+}. Each complex exhibits one reversible, metal-centered reduction and two irreversible, ligand-centered oxidations. Geometric isomerism is suggested by the presence of two infrared absorptions in the Mo=O stretching region.



Yoko Usui, Junko Noma, Masafumi Hirano, Sanshiro Komiya

Inorg. Chim. Acta 309 (2000) 151

C–Si bond cleavage of trihalomethyltrimethylsilane by alkoxo- and aryloxogold or -copper complexes

The C–Si bond cleavage of Me_3SiCX_3 (X = F, Cl) proceeds smoothly by alkoxo- and aryloxogold(I or III) or -copper(I) complexes Au(OR)L (OR = $OCH(CF_3)_2$, OPh), L = PCy_3, PPh_3, PMe_2Ph, PMe_3), *cis*-$AuMe_2(OPh)L$ (L = $PMePh_2$, PEt_3, PMe_2Ph, PMe_3), $Cu(OR)(PPh_3)_3$ (OR = $OCH(CF_3)_2$, OPh) to give trihalomethylgold or -copper complexes $Au(CX_3)L$, *cis*-$AuMe_2(CF_3)L$, and $Cu(CF_3)L_3$ with liberation of the corresponding silyl ether Me_3SiOR

Saija Luukkanen, Matti Haukka, Tapani A. Pakkanen

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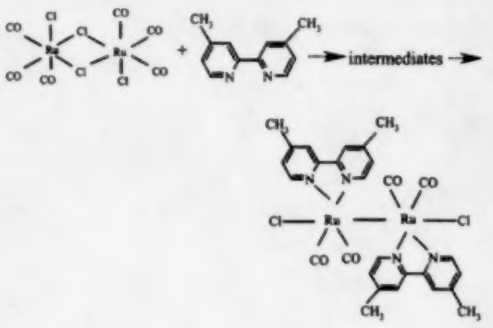
Experimental and theoretical approaches to the reactions of ruthenium-4,4′-dimethyl-2,2′-bipyridine carbonyl complexes

The reactions of ruthenium-4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbpy) carbonyl complexes were investigated by experimental and computational methods. The reaction route from $[Ru(CO)_3Cl_2]_2$ and 4,4′-dmbpy in ethylene glycol proceeded in several consecutive steps to dimeric $[Ru(4,4'\text{-dmbpy})(CO)_2Cl]_2$. The intermediates in each step were isolated and characterized using spectroscopic methods. Total reaction energies were calculated by non-local density functional methods.

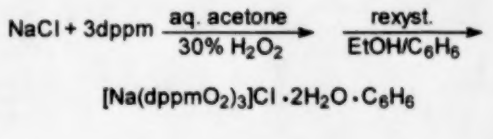


Yan Ding, Phillip E. Fanwick, Richard A. Walton

Inorg. Chim. Acta 309 (2000) 159

An unexpected product isolated during the decomposition of an isomer of $Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3$ — synthesis and structural characterization of $[Na(dppmO_2)_3]Cl{\cdot}2H_2O{\cdot}C_6H_6$

The crystal structure of the sodium complex $[Na(dppmO_2)_3]Cl{\cdot}2H_2O{\cdot}C_6H_6$ ($dppmO_2 = Ph_2P(O)CH_2P(O)Ph_2$) shows it to be isostructural with $[Na(dppmO_2)_3]Br{\cdot}3H_2O$ and $[Na(dppmO_2)_3]I{\cdot}2H_2O{\cdot}C_6H_6$ with a trigonal prismatic geometric about the Na center.

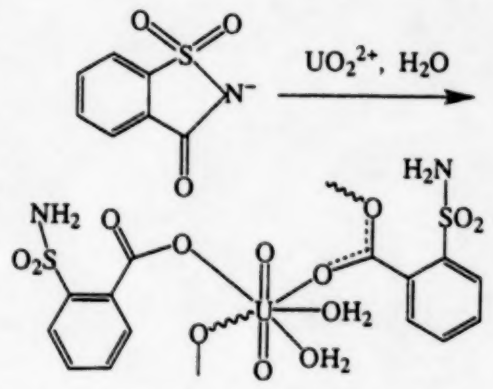


Andrei S. Batsanov, Clair Bilton, Robert M.K. Deng, Keith B. Dillon, Judith A.K. Howard, Harriet Okatch-Nkala

Inorg. Chim. Acta 309 (2000) 163

Preparation of a novel uranyl-*o*-sulfamidobenzoate complex: its crystal and molecular structure at 150 K

A novel uranyl complex of *o*-sulfamidobenzoate has been prepared from a 2:1 reaction of saccharinate ions with uranyl nitrate hexahydrate, leading to ring opening. A single-crystal X-ray diffraction study at 150 K has shown that the compound has a catena structure, with distorted pentagonal bipyramidal coordination of the metal.



Corrigendum

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